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(54) ANTIREFLECTIVE COATING FOR PHOTORESIST COMPOSITIONS

ANTIREFLEXBESCHICHTUNG FÜR PHOTORESISTZUSAMMENSETZUNGEN

REVETEMENT ANTI-REFLECHISSANT POUR COMPOSITIONS DE PHOTORESIST

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EP-A- 0 583 205 **US-A- 5 525 457**

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Description

Background of the Invention

[0001] The present invention relates to novel antireflective coating compositions and their use in forming a thin layer between a reflective substrate and a photoresist coating. Such compositions are especially useful in the fabrication of semiconductor devices by photolithographic techniques.

[0002] Photoresist compositions are used in microlithography processes for making miniaturized electronic components such as in the fabrication of computer chips and integrated circuits. Generally, in these processes, a thin coating of film of a photoresist composition is first applied to a substrate material, such as silicon wafers used for making integrated circuits. The coated substrate is then baked to evaporate any solvent in the photoresist composition and to fix the coating onto the substrate. The baked coated surface of the substrate is next subjected to an image-wise exposure to radiation.

[0003] This radiation exposure causes a chemical transformation in the exposed areas of the coated surface. Visible light, ultraviolet (UV) light, electron beam and X-ray radiant energy are radiation types commonly used today in microlithographic processes. After this image-wise exposure, the coated substrate is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the photoresist.

[0004] The trend towards the minitiarization of semiconductor devices has lead to the use of sophisticated multilevel systems to overcome difficulties associated with such minitiarization The use of highly absorbing antireflective coatings in photolithography is a simpler approach to diminish the problems that result from back reflection of light from highly reflective substrates. Two deleterious effects of back reflectivity are thin film interference and reflective notching. Thin film interference results in changes in critical linewidth dimensions caused by variations in the total light intensity in the resist film as the thickness of the resist changes. Variations of linewidth are proportional to the swing ratio (S) and therefore must be minimized for better linewidth control. Swing ratio is defined by:

$$S = 4(R_1R_2)^{1/2}e^{-\alpha D}$$

where R_1 is the reflectivity at the resist/air or resist/top coat interface,
where R_2 is the reflectivity at the resist/substrate interface,
where α the resist optical absorption coefficient, and
D is the film thickness.

[0005] Antireflective coating function by absorbing the radiation used for exposing the photoresist, that is, reducing R_2 and thereby reducing the swing ratio. Reflective notching becomes severe as the photoresist is patterned over substrates containing topographical features, which scatter light through the photoresist film, leading to linewidth variations, and in the extreme case, forming regions with complete resist loss.

[0006] In the past dyed photoresists have been utilized to solve these reflectivity problems. However, it is generally known that dyed resists only reduce reflectivity from the substrate but do not totally eliminate it. In addition, dyed resists may cause reduction in the lithographic performance of the photoresist, together with possible sublimation of the dye and incompatibility of the dye in resist films. In cases where further reduction or elimination of the swing ratio is required, an antireflective coating is applied prior to coating with the photoresist and prior to exposure. The resist is exposed imagewise and developed. The antireflective coating in the exposed area is then etched, typically in an oxygen plasma, and the resist pattern is thus transferred to the substrate. The etch rate of the antireflective film should be relatively high so that the antireflective film is etched without excessive loss of the resist film during the etch process.

[0007] Antireflective coatings containing a dye for absorption of the light and an organic polymer to give coating properties are known. However, the possibility of sublimation and diffusion of the dye into the photoresist layer during the heating process can make these types of antireflective compositions undesirable.

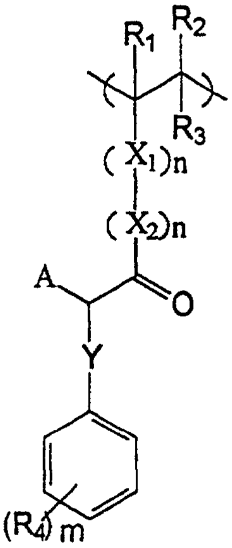
[0008] Polymeric organic antireflective coatings are known in the art as described in EP 583,205 and US 5,525,457. However, these antireflective films are cast from organic solvents, such as cyclohexanone and cyclopentanone. The potential hazards of working with organic solvents, have lead to the development of the antireflective coating composition of the instant invention, where the solid components of the antireflective coating are both soluble and spin castable from solvents having lesser toxicity hazards. The preferred solvents that are known in the semiconductor industry to have low toxicity among others are propylene gycol monomethyl etheracetate (PGMEA), propylene gycol monomethylether (PGME), and ethyl lactate.

[0009] In another embodiment, by the judicious choice of electrophilic substituents and comonomers, the polymer of the present invention is castable from water. Water based coatings are not only preferred but also provide a distinct advantage in the semiconductor industry due to their ease of handling.

[0010] The novel dye functionality of the instant invention, together with the specific types of monomers used, make the instant invention of great significance in the photoresist technology. The antireflective coating gives good coatings and additionally, no intermixing is present between the antireflective coating and the photoresist film. It also has good dry etching properties, which enable a good image transfer from the resist to the substrate and good absorption characteristics to prevent reflective notching and linewidth variations.

Summary of the Invention

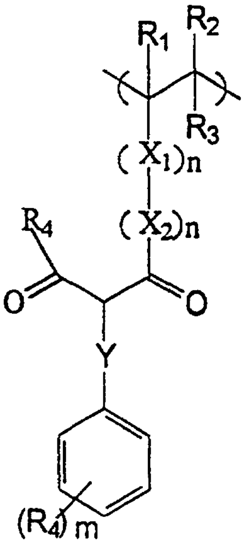
[0011] The present invention relates to a novel antireflective coating composition and a process for its use in photolithography. The polymer of the antireflective coating composition comprises at least one unit with a dye functionality and at least one unit with a crosslinking group. The dye functionality is one that strongly absorbs radiation ranging from about 180nm (nanometer) to about 450nm. The types of dyed monomeric units that can be used are defined by the following structure:



Structure 1

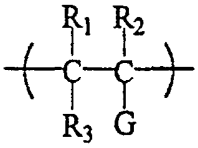
where R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,
X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,
X_2 is S, S(C_1-C_{10}) alkyl, O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),
n=0-2,
A is an electronwithdrawing group, preferrably COR_4, CN or CNZ
R_4 is H. (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z,
NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, alkali metal, ammonium or alkyl ammonium,
Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is
H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy, and
m = 1-5.

[0012] The more preferred structure for the dye unit is,



where R_1-R_3 are independently H, $(C_1$-$C_{10})$ alkyl or $(C_1$-$C_{10})$ alkoxy,
X_1 is C=O, OCO, CONH, O, aryl, $(C_1$-$C_{10})$ alkyl, cyclohexyl, pyridine or pyrollidone,
X_2 is S, $S(C_1$-$C_{10})$ alkyl, O, $O(C_1$-$C_{10})$ alkyl, NH, $N(C_1$-$C_{10})$ alkyl, alkyl, or hydroxyalkyl$(C_1$-$C_{10})$,
n=0-2,
R_4 is H, $(C_1$-$C_{10})$ alkyl, $(C_1$-$C_{10})$ alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z,
NHCOZ, SO_2NZ_2, where Z is H or $(C_1$-$C_{10})$ alkyl, alkali metal, ammonium or alkyl ammonium,
Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, $(C_1$-$C_{10})$ alkyl or $(C_1$-$C_{10})$ alkoxy, and
m = 1-5.

[0013] The unit containing the crosslinking group is defined by the structure,

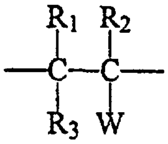


$$-\left(\begin{matrix} R_1 & R_2 \\ | & | \\ C & C \\ | & | \\ R_3 & G \end{matrix}\right)-$$

Structure 2

where G contains the crosslinking functionality and R_1 to R_3 are independently H $(C_1$-$C_{10})$ alkyl or $(C_1$-$C_{10})$ alkoxy, and where the crosslinking groups are typically methylol acrylamides, methacrylamides, acrylamides, ethylene end groups, epoxies, and isocyanates.

[0014] In another preferred embodiment, where the antireflective coating is water soluble, a hydrophilic monomeric unit is also present in the polymer that promotes water solubility in the copolymer and can be represented by the structure:



$$-\begin{matrix} R_1 & R_2 \\ | & | \\ C & C \\ | & | \\ R_3 & W \end{matrix}-$$

where R_1 to R_3 is H, $(C_1$-$C_{10})$ alkyl, $(C_1$-$C_{10})$ alkoxy and W is a hydrophilic group. Examples of the hydrophilic group, W, are given here but are not limited to these:
$O(CH_2)_2$-O-(CH_2)-OH, $O(CH_2)_2$-OH, $(CH_2)_n$-OH (where n=1-4), $COO(C_1$-$C_4)$ alkyl, COOX, SO_3X (where X is H, alkali

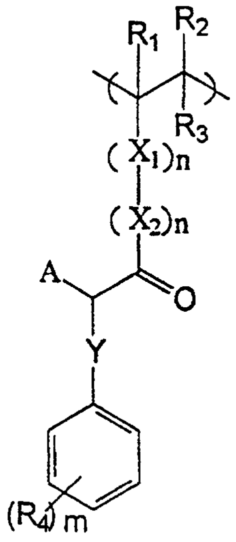
metal, ammonium, alkyl ammonium), $CONHCH_2OH$. Other hyrodophilic vinyl monomers that can also be used in the polymer are, maleic anhydride, fumaric anhydride, vinyl pyridines, and vinyl pyrollidones.

[0015] The invention further comprises a process of forming an image on a substrate. The substrate is coated with the film of the antireflective coating of the instant invention and heated to remove any residual solvent and to insolubilize the coating. A film from a photoresist solution is then formed on top of the antireflective coating and further heated to substantially remove the photoresist solvent. The photoresist film is imagewise exposed through a mask with ultraviolet radiation ranging from about 180nm to about 450nm and processed in an aqueous alkaline developer to give a photoresist pattern. The substrate may be heated prior to and after the development step to give an image of superior quality. The exposed antireflective film can then be dry etched, usually in an oxygen plasma, with the photoresist pattern acting as an etch mask.

Detailed Description of the Invention

[0016] The antireflective compositions of the present invention comprise a polymer obtained by reacting at least one monomer containing a dye functionality and at least one monomer containing a crosslinking group, and where the polymer thus obtained strongly absorbs ultraviolet light having a wavelength in the range of 180nm to about 450nm. The present invention further provides for a process of coating and baking the antireflective coating on a substrate and applying and imaging a photoresist film on top of the antireflective coating, and followed by etching of the antireflective coating.

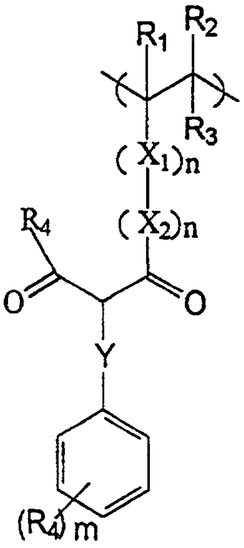
[0017] The polymer of the instant invention is obtained by reacting at least one vinyl monomer containing a dye functionality and at least one vinyl monomer containing a crosslinking group. The dye groups are ones that strongly absorb radiation ranging from about 180nm to about 450nm. The preferred types of dyed monomeric units that can be used are defined by the following structure:



Structure 1

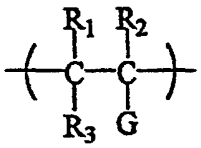
where R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,
X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,
X_2 is S, S(C_1-C_{10}) alkyl, O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),
n=0-2,
A is an electronwithdrawing group, preferrably COR_4, CN or CNZ,
R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z,
NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,
Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy, and
m = 1-5.

[0018] The more preferred structure for the dye unit is,



where R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,
X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,
X_2 is S, S(C_1-C_{10}) alkyl, O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),
n=0-2,
R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z,
NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,
Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy, and
m = 1-5.

[0019] The crosslinking groups present in the antireflective polymer are typically methylol acrylamides, methacrylamides, acrylamides, ethylene end groups, epoxies, isocyanates, but methylol acrylamides and epoxy groups are preferred. The presence of crosslinking groups in the antireflective film are essential to the invention, since the film must be made insoluble in both the solvent of the photoresist and in the developer of the isocyanates, but methylol acrylamides and epoxy groups are preferred. The presence of crosslinking groups in the antireflective film are essential to the invention, since the film must be made insoluble in both the solvent of the photoresist and in the developer of the resist, where the developer is an aqueous alkaline solution. Heating the antireflective film after the coating process induces crosslinking of the polymer and hence makes the coating insoluble in the aqueous developer. However, the crosslinking functionality must be stable in the solution of the antireflective polymer and crosslink when heated at temperatures greater than about 70°C. The crosslinking monomeric unit is represented by the following structure:



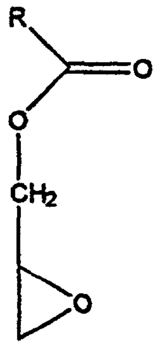
Structure 2

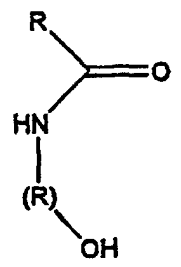
where G contains the crosslinking functionality and R_1 to R_3 is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy.

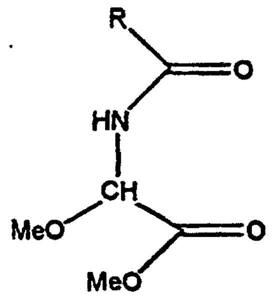
[0020] Specific examples of crosslinking functionality are shown in the following. diagram but are not limited to,


(1)

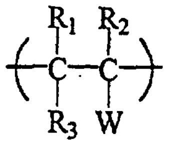

(2)


(3)


(4)


(5)

where (1) is a carbodiimide, (2) an isocyanate or blocked equivalent, (3) glycidyl acrylate or methacrylate, (4) an alkylol acrylamide or methacrylamide and, (5) methyl acrylamidoglycolate methyl ether, R is (C_1-C_{10}) alkyl, and R' is H or (C_1-C_{10}) alkyl.



$$\left(-\underset{R_3}{\overset{R_1}{C}}-\underset{W}{\overset{R_2}{C}}-\right)$$

where R_1 to R_3 are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy and W is a hydrophilic group. Examples of the hydrophilic group, W, are given here but are not limited to these: $O(CH_2)_2$-O-(CH_2)-OH, $O(CH_2)_2$-OH, $(CH_2)_n$-OH (where n=1-4), COO(C_1-C_4) alkyl, COOX, SO_3X (where X is H, alkali metal, ammonium, alkyl ammonium), $CONHCH_2OH$. Other hyrodophilic vinyl monomers that can also be used in the polymer are, maleic anhydride, fumaric anhydride, vinyl pyridines, and vinyl pyrollidones.

[0021] The water soluble antireflective polymer can be synthesized by reacting any number of vinyl monomers containing at least one dye functionality described in Structure 1, any number of vinyl monomers containing at least one crosslinking functionality (Structure 2) and any number of hydrophilic vinyl monomers. Mixtures of different dye monomers, different crosslinking monomers and different hydrophilic monomers can be polymerized to give an antireflective coating with the optimally desired lithographic and physical properties. Other unsaturated monomers can be added to the polymerization mixture that do not greatly effect the function or reduce the aqueous solubility of the antireflective coating. Examples of such unsaturated monomers are, maleic anhydride, vinyl acrylates, vinyl ethers, vinyl acrylamides, vinyl carboxylic acids, vinyl sulphonic acids and N-(3-hydroxyphenylmethacrylamide). Alternatively, the dye can be functionalized to a copolymer to give the polymer of the current invention.

[0022] The antireflective polymer that is soluble in organic solvents can be synthesized by reacting any number of vinyl monomers containing at least one dye functionality described in Structure 1 and any number of vinyl monomers containing at least one crosslinking functionality as described in Structure 2. Mixtures of different dye monomers from Structure 1 with different substituents and different crosslinking monomers from Structure 2 can be polymerized to give an antireflective coating with the desired lithographic and physical properties. The substituents on each of the monomers can be chosen such that the polymer formed from these monomers is soluble in an organic solvent. Other unsaturated monomers can be added to the polymerization mixture that do not greatly effect the function *of* the antireflective coating. Examples of such unsaturated monomers are maleic anhydride, vinyl acrylates and methacrylates, vinyl ethers, vinyl acrylamides, vinyl phenolics, vinyl carboxylic acids, vinyl sulphonic acids and N-(3-Hydroxyphenylmethacrylamide). Alternatively, the dye can be functionalized to a copolymer to give the polymer of the current invention.

[0023] The process used for polymerization can be any of the ones known in the art for polymerizing vinyl polymers, such as, ionic or free radical polymerization. The polymer structure formed can be composed of alternate, block or random copolymers. The weight average molecular weight of the polymer ranges from about 2,500 to about 1,000,000.

[0024] The monomers can be polymerized in a organic solvent, where the solvent is the same as the casting solvent of the antireflective coating, preferrably PGMEA, PGME or ethyl lactate.

[0025] The mole % of the dye containing monomer can range from about 5 to 95, and the mole % of the crosslinking monomer can range from about 1 to about 50 in the final polymer. The water based antireflective coating may contain from about 5 to 95 mole% dye unit, from about 1 to 50 mole% crosslinking unit and from about 1 to 50 mole% of hydrophilic unit. Additionally, the polymer may contain unreacted precursors and/or monomers from the synthetic steps of the preparation of the polymer.

[0026] The antireflective coating composition comprises the polymer of the instant invention and a suitable solvent or mixtures of solvents. Other components may be added to enhance the performance of the coating, e.g. monomeric crosslinking agents, monomeric dyes, lower alcohols, additives to promote crosslinking, acid generators, thermally activated acid generators, surface levelling agents, adhesion promoters, antifoaming agents etc. Examples of crosslinking agents include, but are not limited to, melamines, hydroxy alkyl amides, epoxy and epoxy amine resins, blocked isocyanates, and divinyl monomers. Thermally activated acid generators can be, but are not limited to, predominantly 2,1,4 diazonaphthoquinone esters of multihydroxy phenolic compounds. Monomeric dyes may also be added to the antireflective coating, examples of which are sudan orange, 2,4-dinitronaphthol, curcumin, coumarins and others. to, predominantly 2,1,4 diazonaphthoquinone esters of multihydroxy phenolic compounds. Monomeric dyes may also be added to the antireflective coating, examples of which are sudan orange, 2,4-dinitronaphthol, curcumin, coumarins and others.

[0027] The absorption of the antireflective coating can be optimized for a certain wavelength or ranges of wavelengths by the suitable choice of substituents on the dye functionality. Using substituents that are electron-withdrawing or electron donating generally shifts the absorption wavelength to longer or shorter wavelengths respectively. In addition, the solubility of the antireflective polymer in a particularity preferred solvent can be adjusted by the appropriate choice of substituents on the monomer.

[0028] The polymer of the antireflective coating composition is present in the range of about 1% to about 30% by total weight of solution. The exact weight used is dependent on the molecular weight of the polymer and the film thickness of the coating desired. Typical solvents, used as mixtures or alone, that can be used are propylene glycol monomethyl ether (PGME), propylene glycol monomethyl etheracetate (PGMEA), ethyl lactate, water, cyclopentanone, cyclohexanone, and gamma butyrolactone, but PGME, PGMEA and ethyl lactate or mixtures thereof are preferred. Solvents with a lower degree of toxicity, and good coating and solubility properties are generally preferred.

[0029] Since the antireflective film is coated on top of the substrate and is further subject to dry etching it is envisoned that the film is of sufficiently low metal ion level and purity that the properties of the semiconductor device are not adversely effected. Treatments such as passing a solution of the polymer through an ion exchange column or a combination of anion and cation exchange columns, filteration, and an extraction process can be used to reduce the concentration of metal ions and to reduce particles. Metal ion levels in the polymer below 50ppb each metal are preferred, below 10ppb are more preferred and below 1ppb are even more preferred.

[0030] The antireflective coating composition is coated on the substrate using techniques well known to those skilled in the art, such as dipping, spincoating or spraying. The film thickness of the antireflective coating ranges from about 0.1 micro meter to about 1 micro meter, The coating is further heated on a hot plate or convection oven to remove any residual solvent and to induce the appropriate degree of crosslinking in order to insolubilize the film.

[0031] Photoresists coated over the antireflective film can be any of the types used in the semiconductor industry provided the sensitivity of the photoactive compound in the photoresist matches that of the antireflective coating.

[0032] There are two types of photoresist compositions, negative-working and positive-working. When negative-working photoresist compositions are exposed image-wise to radiation, the areas of the resist composition exposed to the radiation become less soluble to a developer solution (e.g. a cross-linking reaction occurs) while the unexposed areas of the photoresist coating remain relatively soluble to such a solution. Thus, treatment of an exposed negative-working resist with a developer causes removal of the non-exposed areas of the photoresist coating and the creation of a negative image in the coating. Thereby uncovering a desired portion of the underlying substrate surface on which the photoresist composition was deposited.

[0033] On the other hand, when positive-working photoresist compositions are exposed image-wise to radiation, those areas of the photoresist composition exposed to the radiation become more soluble to the developer solution (e.g. a rearrangement reaction occurs) while those areas not exposed remain relatively insoluble to the developer solution. Thus, treatment of an exposed positive-working photoresist with the developer causes removal of the exposed areas of the coating and the creation of a positive image in the photoresist coating. Again, a desired portion of the underlying surface is uncovered.

[0034] Positive working photoresist compositions are currently favored over negative working resists because the former generally have better resolution capabilities and pattern transfer characteristics. Photoresist resolution is defined as the smallest feature which the resist composition can transfer from the photomask to the substrate with a high degree of image edge acuity after exposure and development. In many manufacturing applications today, resist resolution on the order of less than one micro meter are necessary. In addition, it is almost always desirable that the developed photoresist wall profiles be near vertical relative to the substrate. Such demarcations between developed and undeveloped areas of the resist coating translate into accurate pattern transfer of the mask image onto the substrate. This becomes even more critical as the push toward miniaturization reduces the critical dimensions on the devices.

[0035] Positive-acting photoresists comprising novolak resins and quinone-diazide compounds as photoactive compounds are well known in the art. Novolak resins are typically produced by condensing formaldehyde and one or more multi-substituted phenols, in the presence of an acid catalyst, such as oxalic acid. Photoactive compounds are generally obtained by reacting multihydroxyphenolic compounds with naphthoquinone diazide acids or their derivatives. The sensitivity of these types of resists typically ranges from about 350nm to 440nm.

[0036] Photoresists sensitive to short wavelengths, between about 180nm and about 300nm can also be used. These resists normally comprise polyhydroxystyrene or substituted polyhydroxystyrene derivatives, a photoactive compound, and optionally a solubility inhibitor. The following references exemplify the types of photoresists used US 4,491,628, US 5,069,997 and US 5,350,660.

[0037] The process of the instant invention further comprises coating a substrate with the novel antireflective coating and heating on a hotplate or convection oven at a sufficiently high temperature for sufficient length of time to remove the coating solvent and crosslink the polymer to a sufficient extent so as not to be soluble in the coating solution of the photoresist or in the aqueous alkaline developer. The preferred range of temperature is from about 70°C to about 250°C. If the temperature is below 70°C then insufficient loss of solvent or insufficient degree of crosslinking takes place and at temperatures above 250°C the polymer may become chemically unstable. A film of photoresist is then coated on top of the antireflective coating and baked to substantially remove the photoresist solvent. The photoresist is imagewise exposed and developed in an aqueous developer to remove the treated resist. An optional heating step can be incorporated into the process prior to development and after exposure. The process of coating and imaging photoresists is well known to those skilled in the art and is optimized for the specific type of resist used. The patterned substrate can then be dry etched in a suitable etch chamber to remove the exposed portions of the antireflective film, with the remaining photoresist acting as an etch mask.

[0038] An intermediate layer may be placed between the antireflective coating and the photoresist to prevent intermixing, and is envisioned as lying within the scope of this

[0039] The following specific examples will provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

Examples

Polymer 1 - Example 1. Preparation of the diazonium salt of ethyl-4-aminobenzoate

[0040] Ethyl 4-aminobenzoate (50.57 g, 0.3 mol) was dissolved in 61 ml (0.75 mol) of concentrated hydrochloric acid and 600 ml of methanol contained in a 1000 ml roundbottom flask. The flask was then immersed in a bath of crushed ice, and cooled until the temperature of the solution was below 3°C. The solution turned into a white suspension. Diazotization was then facilitated by the addition of 33.3 g (0.31 mol) *tert*-butyl nitrite at a temperature below 5°C. The diazonium solution was then stirred in an ice-water bath for about 1 hour. The product forms as a yellow solution in methanol and was not isolated, but used as a reagent in Example 2.

Polymer 1 - Example 2. Preparation of the methacrylate monomer

[0041] 2-(Methacryloyloxy)ethyl acetoacetate (66.25 g, 0.3 mol) and triethylamine (76.66 g, 0.75 mol) were added to methanol (1500 ml) and the solution stirred and cooled below 5°C in an ice-water bath. To this solution, the cold diazonium salt solution, formed in Example 1, was then slowly added, while the temperature was maintained between 5°C to 10°C. The reaction mixture was allowed to stir for 4 hours while warming to room temperature resulting in the formation of the product as a red suspension. This was then filtered, washed with methanol and dried under vacuum to yield 89.7 g (77%) of yellow product.

Polymer 1 - Example 3. Preparation of Copolymer

[0042] The methacrylate monomer formed in Example 2 (21.47 g, 0.055 mol) was dissolved in 125 ml of γ-butyrolactone solvent. The solution was warmed to 65°C while stirred. On complete dissolution, the solution was degassed by vigorously bubbling argon, via an inlet needle in a sealed rubber septum, through the solution for about 2 hours. N-(Hydroxymethyl)acrylamide (0.899 ml, 4.58 mmol) and methyl methacrylate (3.47 ml, 32 mmol) were then injected into the solution through the septum and the polymerization mixture was further degassed for 30 minutes. An aliquot from a solution of AIBN (0.1843 g, 0.92 mmol, 1mol % total monomer) in γ-butyrolactone (1.5 ml) was then injected and the solution degassed further for 30 minutes. In total, 2 aliquots were added at intervals of 5 hours. Both inlet and outlet needles were then removed and the sealed vessel allowed to stir at 65°C for 20 hours. This solution was then diluted with ethyl acetate (500ml) then precipitated into a fivefold excess of 2-propanol. The polymer forms as a yellow solid (23.25 g) which was then collected by filtration and dried. The yield was 92%.

Polymer 2 - Example 4. Preparation of the diazonium salt of 4-aminobenzoic acid.

[0043] 4-Aminobenzoic acid (13.85 g, 0.1 mol) was dissolved in 20 ml (0.25 mol) of concentrated hydrochloric acid and 150 ml of methanol contained in a 300 ml roundbottom flask. The flask was then immersed in a bath of crushed ice, and cooled until the temperature of the solution was below 3°C. The solution turned into a white suspension. Diazotization was then facilitated by the addition of 11.82 g (0.11 mol) *tert*-butyl nitrite at a temperature below 5°C. The diazonium solution was then stirred in an ice-water bath for about 1 hour. The product forms as a off white suspension in methanol and was not isolated, but used as a reagent in Example 5.

Polymer 2 - Example 5. Preparation of the methacrylate monomer.

[0044] 2-(Methacryloyloxy)ethyl acetoacetate (22.08 g, 0.1 mol) and triethylamine (25.55 g, 0.25 mol) were added to methanol (200 ml) and the solution stirred and cooled below 5°C in an ice-water bath. To this solution, the cold diazonium salt solution formed in Example 4, was then slowly added, while the temperature was maintained between 10 to 20°C. The reaction mixture was allowed to stir for 2.5 hours while warming to room temperature resulting in the formation of the product as a yellow suspension. This was poured into 2000ml of distilled water, then filtered, and dried under vacuum to yield a yellow solid product.

Polymer 2 - Example 6. Preparation of Copolymer.

[0045] The methacrylate monomer formed in Example 5 (5.25 g, 0.02 mol) was dissolved in 35 ml of γ-butyrolactone solvent. The solution was warmed to 65°C while stirred. On complete dissolution, the solution was degassed by vigorously bubbling argon, via an inlet needle in a sealed rubber septum, through the solution for about 2 hours. N-(hydroxymethyl)acrylamide (1.53 g, 0.012 mol) and methyl methacrylate (1.2 g, 0.12 mol) were then injected into the solution through the septum and the polymerization mixture was further degassed for 30 minutes. An aliquot from a solution of AIBN (0.6138 g, 3.66 mmol, 1mol % total monomer) in γ-butyrolactone (3.5 ml) was then injected and the solution degassed further for 30 minutes. In total, 2 aliquots were added at intervals of 5 hours. Both inlet and outlet needles were then removed and the sealed vessel allowed to stir at 65°C for 20 hours. This solution was then diluted with ethyl acetate (500ml) then precipitated into a fivefold excess of 2-propanol. The polymer forms as a yellow solid which was then collected by filtration and dried.

Polymer 3 - Example 7. Preparation of Copolymer.

[0046] The methacrylate monomer formed in Example 2 (21.47 g, 55 mmol) was dissolved in 125 ml of γ-butyrolactone solvent. The solution was warmed to 65°C while stirred. On complete dissolution, the solution was degassed by vigorously bubbling argon, via an inlet needle in a sealed rubber septum, through the solution for about 2 hours. Methyl 2-acrylamido-2-methoxyacetate (1.94 g, 11 mmol) and methyl methacrylate (4.45 g, 44 mmol) were then injected into the solution through the septum and the polymerization mixture was further degassed for 30 minutes. An aliquot from a solution of AIBN (0.1843 g, 0.92 mmol, 1mol % total monomer) in γ-butyrolactone (1.5 ml) was then injected and the solution degassed further for 30 minutes. In total, 2 aliquots were added at intervals of 5 hours. Both inlet and outlet needles were then removed and the sealed vessel allowed to stir at 65°C for 20 hours. This solution was then diluted with ethyl acetate (500ml) then precipitated into a fivefold excess of 2-aliquots were added at intervals of 5 hours. Both inlet and outlet needles were then removed and the sealed vessel allowed to stir at 65°C for 20 hours. This solution was then diluted with ethyl acetate (500ml) then precipitated into a fivefold excess of 2-propanol. The polymer forms as a yellow solid (20.82 g) which was then collected by filtration and dried. The yield was 75%.

Example 8

[0047] To a solution of 3.5 grams of the polymer from Example 3(Polymer 1) in 46.5 grams of PGMEA was added 0.035 grams of 2,1,4-diazonaphthoquinonesulfonic esters. The solution was filtered with 0.2 μm PTFE filter, spin coated on a 10.16 cm (4") silicon wafer, and baked on a hot plate at 170 °C for 60 seconds to achieve a thickness of about 2000Â. The coated wafers were immersed in-various resist casting solvents such as PGMEA, 85/15 ethyl lactate (EL) /n-Butyl Acetate (n-BA) solvent mixture as well as in AZ® 300 MIF developer (available from Hoechst Celanese Corporation, 70 Meister Ave., Somerville, NJ 08876). The film thickness before and after immersion were measured with a NANOSPEC-AFT. The extent of interlayer mixing between the polymer and the solvent was determined by the changes of the polymer film thickness as listed in the following table.

Table 1

Solvent	T_1	T_2	T_3	T4
PGMEA	2030Å	2029Å	2027Å	2028Å
85/15 EL/>BA	2024Å	2029Å	2021Å	2023Å

where

T_1: polymer film thickness after spin coating
T_2 : polymer film thickness after immersion in the photoresist solvent for 30 seconds
T_3 : polymer film thickness after softbaked at 90°C for 90 seconds
T_4: polymer film thickness after immersion in the AZ® 300 MIF developer for 35 seconds

[0048] The process condition described for T_1 to T_4 mimic a typical coating and developing procedure of a positive photoresist on a bottom antireflective coating. It is clear that the solubility of the polymer of present invention with typical photoresist casting solvent and developer is negligible.

Example 9

[0049] To a solution of 3.5 grams of the polymer from Example 3(Polymer 1) in 46.5 grams of PGMEA was added 0.52 grams of CYMEL® 303 and 0.05 grams of CYCAT® 296-6 (both available from Cytec Industries Inc.) The solution was filtered with 0.2 µm PTFE filter, spin coated on a 10.16 cm (4") silicon wafer, and baked on a hot plate at 170°C for 60 seconds. The coated wafers were immersed in PGMEA and EL for 20 seconds and in AZ® 300 MIF developer for 40 seconds. After spin dried, no changes on film thickness were observed.

Example 10

[0050] The polymer solutions formulated in Examples 8 and 9 were spin coated on several 10.16cm (4") silicon wafer and baked on a hot plate at 170°C for 60 seconds to give a thickness of 2000 Â. The wafers were then coated with AZ® 7805 (available from Hoechst Celanese Corporation, 70 Meister Ave., Somerville, NJ 08876) and baked using a temperature of 90°C for 90 seconds to give thickness from 0.5 µm (micrometers). A 10.16 cm (4") silicon wafer coated with 5000 Â AZ® 7805 photoresist and baked at 90°C on a hot plate for 60 seconds was used as the reference. These wafers were imagewise exposed with a NIKON® 0.54 NA i-line stepper using a reticle contains line size from 0.2 µm to 1.0 µm and a program that directs the stepper to print a 15x21 focus/exposure matrix with dose increments of 2 mJ/cm^2 and focus increment of 0.2 µm. The exposed wafers were baked at 110°C for 60 seconds and puddle developed with AZ® 300 MIF developer for 35 seconds.. The resist pattern generated on these wafers were evaluated by a Hitachi S-4000 field emission scanning electron microscope. Table 2 shows the comparison of AZ® 7805 on the bottom antireflective coatings of the present invention versus AZ® 7805 on a bare silicon wafer.

Table 2

Bottom Coating	DTP (mJ/cm2)	Resolution	Standing Wave
Example 8	210	0.28 µm	No
Example 9	205	0.28 µm	No
none	195	0.38 µm	Severe
DTP is the dose to print.			

The bottom polymer coatings of the present invention clearly improve the resolution and effectively eliminate the standing waves, that is, reflectivity, without sacrificing photosensitivity.

Example 11

[0051] To a solution of 3.5 grams of the polymer from Example 7 (Polymer 3) in 46.5 grams of PGMEA was added

0.52 grams of CYMEL® 303 and 0.05 grams of CYCAT® 296-6. The solution was filtered with 0.2 µm PTFE filter, spin coated on a 10.16cm (4") silicon wafer, and baked on a hot plate at 170 °C for 60 seconds to give a thickness of 2000 Â. The wafers were then coated with AZ® 7805 and baked using a temperature of 90°C for 90 seconds to give thickness from 0.5 µm (micrometers). A 10.16 cm (4") silicon wafer coated with 5000 Â AZ® 7805 photoresist and baked at 90°C on a hot plate for 60 seconds was used as the reference. These wafers were imagewise exposed with a NIKON® 0.54 NA i-line stepper using a reticle contains line size from 0.2 µm to 1.0 µm and a program that directs the stepper to print a 15x21 focus/exposure matrix with dose increments of 2 mJ/cm^2 and focus increment of 0.2 µm. The exposed wafers were baked at 110°C for 60 seconds and puddle developed with AZ® 300 MIF developer for 35 seconds. The resist patterns generated on these wafers were evaluated by a Hitachi S-4000 field emission scanning electron microscope. Table 3 shows the comparison of AZ® 7805 on the bottom polymer coating of the present invention versus AZ® 7805 on a bare silicon wafer.

Table 3

Bottom Coating	DTP (mJ/cm2)	Resolution	Standing Wave
Example 11	230	0.28 µm	No
none	195	0.38 µm	Severe

[0052] The polymer coating described in this example clearly shows improved resolution compared to photoresist without the bottom antireflective coating and is capable of eliminating the standing waves, that is, reflectivity, without significantly sacrificing the photosensitivity.

Example 12. Swing Ratio Reduction Test

[0053] The swing ratio of a photoresist is closely related to the linewidth variation of the photoresist pattern over a highly reflective substrate or topography commonly encountered in a semiconductor device manufacturing. The lower the swing ratio, the better the linwidth control over reflective substrate or topography. The swing ratio was calculated by the equation:

$$(Emax - Emin)/(Emax + Emin)$$

where Emax and Emin corresponding to the dose-to-clear of a resist thickness at the maximum and minimum on a swing curve. Swing curve were generated by ploting the dose requied to clear a resist film after developement as a function of the resist thickness.

[0054] Several 10.16 cm (4") wafers were coated with AZ® 7805 to give thickness from 0.5 µm to 1.0 µm using a soft bake temperature of 90°C for 90 seconds. These wafers were imagingwise exposed with a NIKON 0.54 NA i-line stepper, then baked at 110°C for 60 seconds and puddle developed with AZ® 300 MIF developer for 35 seconds. The minimum dose required to clear the film is plotted as a function of corresponding resist thickness, a sinusoidal curve thus obtain is called the swing curve.

[0055] The Swing ratio of the polymers of Examples in 9 and 11 are given in the following table.

Table 4

Sample	% Swing Reduction
AZ® 7805	0
Example 9(Polymer 1)	92.05
Example 11(Polymer 3)	93.86

[0056] It's clearly shown that both of the present invention effectively reduce the swing curve ratio by about 92%.

Polymer 4 - Example 13

[0057] 2-(Methacryloyloxy)ethyl acetoacetate (57.42g, 0.26mol) and diethylene glycol monovinyl ether (18.5g, 0.14 mol) were dissolved in 330 ml of γ-butyrolactone solvent. The solution was warmed to 65°C while being stirred. The solution was then degassed by vigorously bubbling argon, via an inlet needle in a sealed rubber septum, through the solution for about 2 hours. An aliquot from a solution of AIBN (0.657 g, 4 mmol, lmol % total monomer) in γ-butyrolactone

(3.5 ml) was then injected and the solution degassed further for 30 minutes. In total, 2 aliquots were added at intervals of 5 hours. Both inlet and outlet needles were then removed and the sealed vessel allowed to stir at 65 °C for 20 hours The product formed was then used as a reagent in Example 15.

Polymer 4 - Example 14

[0058] To a solution of tetramethyl ammonium hydroxide in water (25 % solids) (72 ml, 0.2 mol) and water (150ml) was added sulfanilic acid (34.99g, 0.2 mol), followed by isobutyl nitrite (26 ml. 0.21 mol) and the resultant suspension temperature maintained below 10°C. A solution of HCl (37.8 wt % in water) (32.5 ml, 0.4 mol) was added to water (35 ml) and the solution slowly added to the reaction mixture, forming the diazonium salt, which was then transferred to a pressure equalizing dropping funnel and used as a reagent in Example 15.

Polymer 4 - Example 15

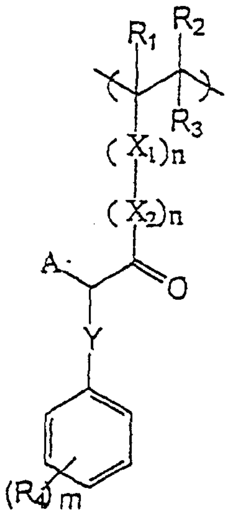
[0059] To the polymer solution formed in Example 13, was added DMSO (500 ml) and tetramethyl ammonium hydroxide solution in water (144 ml, 0.4 mol), and the mixture stirred while cooling to below 10°C. To this, was then added, dropwise, the product from Example 14, and the resultand red solution allowed to stir at room temperature overnight. The solution was then precipitated into 2-propanol (2000 ml), allowing the polymer to form as a solid product.

[0060] The polymer was dissolved in water and coated on a silicon wafer. The polymer functioned as a bottom antireflective coating for a photoresist composition.

Claims

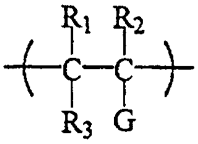
1. An antireflecting coating composition for use in photolithography, comprising

a) a polymer comprising at least one dye unit having a structure,



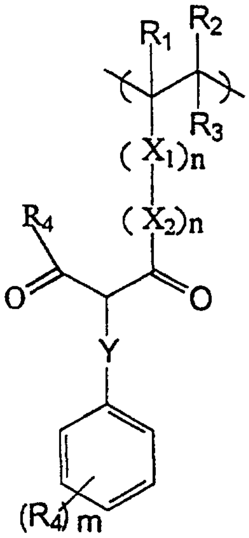
where R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,
X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,
X_2 is S, S(C_1-C_{10}) alkyl, O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),
n=0-2,
A is an electronwithdrawing group, preferably COR_4, CN or CNZ,
R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, alkali metal, ammonium or alkyl ammonium,
Y is a conjugated moiety N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,
m = 1-5, and

at least one unit capable of crosslinking the polymer having a structure



where G contains a crosslinking functionality and R_1 to R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy, and
b) a suitable solvent.

2. The antireflective coating composition according to claim 1, wherein the dye unit has a structure



where R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,
X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,
X_2 is S, $S(C_1-C_{10})$ alkyl, O, $O(C_1-C_{10})$ alkyl, NH, $N(C_1-C_{10})$ alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),
n=0-2,
R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2; SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,
Y is a conjugated moiety N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy, and
m = 1-5.

3. The antireflective composition according to claim 1, wherein the solvent comprises a mixture of organic solvents.

4. The antireflective composition according to claim 1, wherein the solvent is selected from a group consisting of propylene glycol monomethyl ether, propylene glycol monomethyl etheracetate, ethyl lactate, heptanone, cyclopentanone, cyclohexanone, and gamma butyrolactone.

5. The antireflective composition according to claim 1, wherein the solvent comprises water.

6. The antireflective composition according to claim 1, wherein the crosslinking group is selected from a group consisting of carbodiimide, isocyanate, blocked isocyanate, glycidyl methacrylate, alkylol acrylamide, alkylol methacrylamide and methyl acrylamidoglycolate.

7. The antireflective composition according to claim 1, wherein Y in the dye unit is an azo moiety.

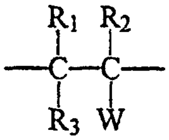
8. The antireflective composition of claim 1, wherein the dye unit ranges from about 5 to about 95 mole percent and the crosslinking unit ranges from about 1 to about 50 mole percent of the polymer.

9. The antireflective composition according to claim 1, wherein the polymer further comprises one or more vinyl monomers that are nonabsorbing and noncrosslinking.

10. The antireflective composition according to claim 9, wherein the vinyl monomer is selected from a group consisting of maleic anhydride, vinyl acrylates, vinyl phenolics, vinyl ethers, vinyl acrylamides, vinyl carboxylic acids, vinyl sulphonic acids and N-(3-Hydroxyphenylmethacrylamide).

11. The antireflective composition according to claim 1, further comprising at least one unit derived from a hydrophilic vinyl monomer or a vinyl monomer capable of becoming hydrophilic.

12. The antireflective composition according to claim 11, where the hydrophilic vinyl monomer has a structure:



$$-\underset{R_3}{\overset{R_1}{C}}-\underset{W}{\overset{R_2}{C}}-$$

where R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy and W is a hydrophilic group.

13. The aqueous antireflective composition according to claim 12, wherein the hydrophilic group is selected from a group consisting of $O(CH_2)_2$-O-(CH_2)-OH, $O(CH_2)_2$-OH, $(CH_2)_n$-OH (where n=1-4), COO(C_1-C_4)alkyl, COOX, SO_3X (where X is H, alkali metal. ammonium, alkyl ammonium) and $CONHCH_2OH$.

14. The antireflective composition according to claim 11, where the hydrophilic vinyl monomer is selected from a group consisting of maleic anhydride, fumaric anhydride, vinyl pyridines,and vinyl pyrollidones.

15. The antireflective composition according to claim 11, wherein the dye unit ranges from about 5 to about 95 mole percent, the crosslinking unit ranges from about 1 to about 50 mole percent and the hydrophilic vinyl monomer ranges from about 1 to about 50 mole percent of the polymer. about 50 mole percent and the hydrophilic vinyl monomer ranges from about 1 to about 50 mole percent of the polymer.

16. The antireflective composition according to claim 1, further comprising a dye.

17. The antireflective composition according to claim 1, further comprising a crosslinking agent.

18. The antireflective composition according to claim 1, further comprising an acid.

19. The antireflective composition according to claim 1, further comprising a heat generated acid.

20. The antireflective composition according to claim 19, wherein the acid is a diazo naphthoquinone ester of a multihydroxybenzophenone.

21. The antireflective composition according to claim 1, wherein the polymer has a weight average molecular weight in the range of about 2,500 to about 1,000,000.

22. The antireflective composition according to claim 1, wherein the metal ion level in the polymer is less than 50ppb each metal ion.

23. The process of forming an image on a substrate comprising the steps of:

a) coating the substrate with the antireflective coating composition of claim 1,
b) heating the antireflective coating,
c) coating a photoresist solution on top of the antireflective coating,
d) heating the photoresist coating to substantially remove solvent from the photoresist coating,

e) imagewise exposing the photoresist coating,
f) developing an image using an aqueous alkaline developer,
g) optionally, heating the substrate prior to and after development,

24. The process of claim 23, wherein the photoresist solution comprises a novolak resin, a photosensitive compound and a solvent.

25. The process of claim 23, wherein the photoresist solution comprises a substituted polyhydroxystyrene, a photoactive compound and a solvent.

26. The process of claim 23, wherein the photoresist solution comprises polyhydroxystyrene, a photoactive compound, a dissolution inhibitor and a solvent.

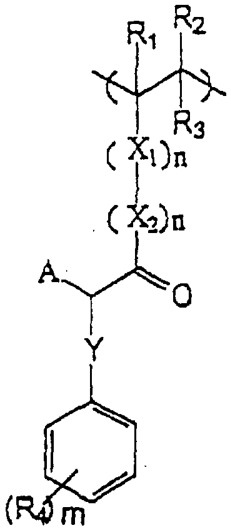
27. The process of claim 23, wherein the heating temperature for the antireflective coating ranges from about 70°C to about 250°C.

28. The process of claim 23, wherein the developer is an aqueous solution of metal ion free alkaline hydroxide.

Patentansprüche

1. Reflexionsvermindernde Beschichtungszubereitung zur Verwendung in der Photolithographie, bestehend aus

a) einem Polymer, das mindestens eine Farbstoffeinheit mit folgender Struktur enthält:



wobei R_1 - R_3, unabhängig voneinander, H, $(C_1$-$C_{10})$-Alkyl oder $(C_1$-$C_{10})$-Alkoxy sind,

X_1 C=O, OCO, CONH, O, Aryl, $(C_1$-$C_{10})$-Alkyl, Cyclohexyl, Pyridin oder Pyrrolidon ist,

X_2 S, $S(C_1$-$C_{10})$-Alkyl, O, $O(C_1$-$C_{10})$-Alkyl, NH, $N(C_1$-$C_{10})$-Alkyl, Alkyl oder Hydroxyalkyl$(C_1$-$C_{10})$ ist,

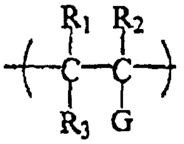
n 0 - 2 ist,

A eine Elektronenakzeptorgruppe ist, bevorzugt COR_4, CN oder CNZ,

R_4 H, $(C_1$-$C_{10})$-Alkyl, $(C_1$-$C_{10})$-Alkoxy, Nitro, Halogenid, Cyano, Aryl, Alkylaryl, Alkenyl, Dicyanovinyl oder SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2 ist, wobei Z H oder $(C_1$-$C_{10})$-Alkyl, Alkalimetall, Ammonium oder Alkylammonium ist, Y eine konjugierte Komponente N=N, CW=CW, CW=N oder N=CW ist, wobei W H, (C_1-C_{10})-Alkyl oder (C_1-C_{10})-Alkoxy ist,

m 1 - 5 ist und

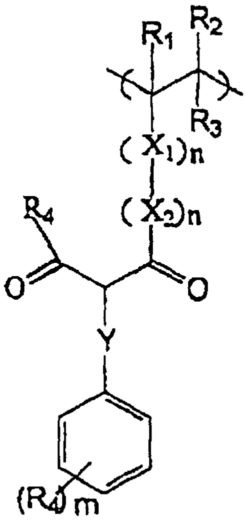
mindestens eine die Vernetzung des Polymers bewirkende Einheit die Struktur



hat, wobei G eine vernetzende Gruppe enthält und R_1 - R_3, unabhängig voneinander, H, (C_1-C_{10})-Alkyl oder (C_1-C_{10})-Alkoxy sind;

b) einem geeigneten Lösungsmittel.

2. Reflexionsvermindernde Beschichtungszubereitung gemäß Anspruch 1, wobei die Farbstoffeinheit folgende Struktur hat



wobei R_1 - R_3, unabhängig voneinander, H, (C_1-C_{10})-Alkyl oder (C_1-C_{10})-Alkoxy sind,

X_1 C=O, OCO, CONH, O, Aryl, (C_1-C_{10})-Alkyl, Cyclohexyl, Pyridin oder Pyrrolidon ist,

X_2 S, S(C_1-C_{10})-Alkyl, O, O(C_1-C_{10})-Alkyl, NH, N(C_1-C_{10})-Alkyl, Alkyl oder Hydroxyalkyl(C_1-C_{10}) ist,

n 0 - 2 ist,

R_4 H, (C_1-C_{10})-Alkyl, (C_1-C_{10})-Alkoxy, Nitro, Halogenid, Cyano, Aryl, Alkylaryl, Alkenyl, Dicyanovinyl oder SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2 ist, wobei Z H oder (C_1-C_{10})-Alkyl ist,

Y eine konjugierte Komponente N=N, CW=CW, CW=N oder N=CW ist, wobei W H, (C_1-C_{10})-Alkyl oder (C_1-C_{10})-Alkoxy ist und

m 1 - 5 ist.

3. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei das Lösungsmittel aus einem Gemisch organischer Lösungsmittel bestehen kann.

4. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei das Lösungsmittel aus einer Gruppe von Substanzen gewählt wird, die aus Propylenglycolmonomethylether, Propylenglycolmonomethyletheracetat, Ethyllactat, Heptanon, Cyclopentanon, Cyclohexanon und γ-Butyrolacton besteht.

5. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei das Lösungsmittel Wasser sein kann.

6. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei die vernetzende Komponente aus einer Gruppe von Substanzen gewählt wird, die aus Carbodiimid, Isocyanat, blockiertem Isocyanat, Glycidylmethacrylat, Alkylolacrylamid, Alkylolmethacrylamid und Methylacrylamidoglycolat besteht.

7. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei Y in der Farbstoffeinheit eine Azokomponente ist.

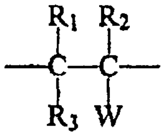
8. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei das Polymer zu ca. 5 bis ca. 95 Molprozent aus der Farbstoffeinheit und zu ca. 1 bis ca. 50 Molprozent aus der vernetzenden Komponente besteht.

9. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei das Polymer zusätzlich ein oder mehrere Vinylmonomere enthält, die nicht absorbierend sind und keine Vernetzung herbeiführen.

10. Reflexionsvermindernde Zubereitung gemäß Anspruch 9, wobei das Vinylmonomer aus einer Gruppe von Substanzen gewählt wird, die aus Maleinsäureanhydrid, Vinylacrylaten, Vinylphenolen, Vinylethem, Vinylacrylamiden, Vinylcarbonsäuren, Vinylsulfonsäuren und N-(3-Hydroxyphenylmetharcrylamid) besteht.

11. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, die zusätzlich mindestens eine weitere, von einem hydrophilen Vinylmonomer oder einem Vinylmonomer, das hydrophil werden kann, abgeleitete Komponente besitzt.

12. Reflexionsvermindernde Zubereitung gemäß Anspruch 11, wobei das hydrophile Vinylmonomer folgende Struktur hat:



$$-\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{W}{C}}-$$

wobei R_1 - R_3, unabhängig voneinander, H, $(C_1\text{-}C_{10})$-Alkyl oder $(C_1\text{-}C_{10})$-Alkoxy sind und W eine hydrophile Gruppe ist.

13. Wäßrige, reflexionsvermindernde Zubereitung gemäß Anspruch 12, wobei die hydrophile Gruppe aus einer Gruppe von Substanzen gewählt wird, die aus $O(CH_2)_2\text{-}O\text{-}(CH_2)\text{-}OH$, $O(CH_2)_2\text{-}OH$, $(CH_2)_n\text{-}OH$ (wobei n = 1 - 4), COO $(C_1\text{-}C_4)$-Alkyl, COOX, SO_3X (wobei X H, ein Alkalimetall, Ammonium oder Alkylammonium ist) und $CONHCH_2OH$ besteht.

14. Reflexionsvermindernde Zubereitung gemäß Anspruch 11, wobei das hydrophile Vinylmonomer aus einer Gruppe von Substanzen gewählt wird, die aus Maleinsäureanhydrid, Fumarsäureanhydrid, Vinylpyridinen und Vinylpyrrolidonen besteht.

15. Reflexionsvermindernde Zubereitung gemäß Anspruch 11, wobei das Polymer zu ca. 5 bis ca. 95 Molprozent aus der Farbstoffeinheit, zu ca. 1 bis ca. 50 Molprozent aus der vernetzenden Komponente und zu ca. 1 bis ca. 50 Molprozent aus dem hydrophilen Vinylmonomer besteht.

16. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, die zusätzlich einen Farbstoff enthält.

17. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, die zusätzlich eine vernetzende Komponente enthält.

18. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, die zusätzlich eine Säure enthält.

19. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, die zusätzlich eine unter der Einwirkung von Wärme entstehende Säure enthält.

20. Reflexionsvermindernde Zubereitung gemäß Anspruch 19, wobei die Säure ein Diazonaphthochinonester eines Multihydroxybenzophenons ist.

21. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei das Polymer eine massegemittelte Molekülmasse von ca. 2500 bis ca. 1000000 hat.

22. Reflexionsvermindernde Zubereitung gemäß Anspruch 1, wobei der Gehalt des Polymers an Metallionen unter jeweils 50 ppb liegt.

23. Verfahren zur Herstellung einer Abbildung auf einem Träger, das aus folgenden Schritten besteht:

a) Beschichten des Trägers mit der reflexionsvermindernden Beschichtungszubereitung gemäß Anspruch 1;

b) Erwärmen der reflexionsvermindernden Beschichtung;

c) Aufbringen der Photoresistlösung auf die reflexionsvermindernde Beschichtung;

d) Erwärmen der Photoresistbeschichtung zur praktisch vollständigen Entfernung des Lösungsmittels aus der Photoresistbeschichtung;

e) abbildungsgemäße Belichtung der Photoresistbeschichtung;

f) Entwicklung einer Abbildung mit einem wäßrig-alkalischen Entwickler;

g) wahlweise Erwärmen des Trägers vor und nach der Entwicklung;

h) Trockenätzen der reflexionsvermindernden Beschichtung.

24. Verfahren gemäß Anspruch 23, wobei die Photoresistlösung aus einem Novolakharz, einer lichtempfindlichen Verbindung und einem Lösungsmittel besteht.

25. Verfahren gemäß Anspruch 23, wobei die Photoresistlösung aus einem substituierten Polyhydroxystyrol, einer lichtempfindlichen Verbindung und einem Lösungsmittel besteht.

26. Verfahren gemäß Anspruch 23, wobei die Photoresistlösung aus Polyhydroxystyrol, einer lichtempfindlichen Verbindung, einem Lösungshemmstoff und einem Lösungsmittel besteht.

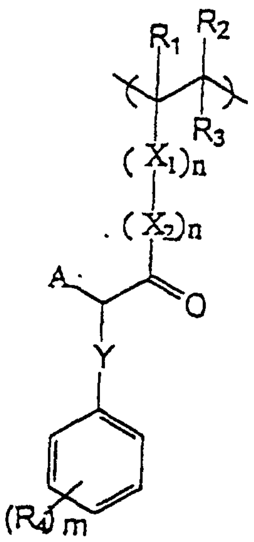
27. Verfahren gemäß Anspruch 23, wobei die Heiztemperatur für die reflexionsvermindernde Beschichtung ca. 70°C bis ca. 250°C beträgt.

28. Verfahren gemäß Anspruch 23, wobei der Entwickler eine wäßrige Lösung eines metallionenfreien, alkalischen Hydroxids ist.

Revendications

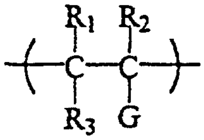
1. Composition de revêtement anti-réfléchissant pour une utilisation en photolithographie, comprenant:

a) un polymère comprenant au moins un motif de colorant ayant une structure:



dans laquelle R_1 à R_3 représentent, indépendamment les uns des autres, H, un groupe alkyle en C_1 à C_{10} ou un groupe alcoxy en C_1 à C_{10};
X_1 est C=O, OCO, CONH, O, un groupe aryle, alkyle en C_1 à C_{10}, cyclohexyle, pyridine ou pyrolidone;
X_2 est S, un groupe S-alkyle en C_1 à C_{10}, O, un groupe O-alkyle en C_1 à C_{10}, NH, un groupe N-alkyle en C_1 à C_{10} un groupe alkyle ou un groupe hydroxyalkyle en C_1 à C_{10};
n= 0 à 2
A est un groupe attracteur d'électrons, de préférence COR_4, CN ou CNZ;
R_4 représente H, un groupe alkyle en C_1 à C_{10}, un groupe alcoxy en C_1 à C_{10}, un groupe nitro, halogénure, cyano, aryle, alkylaryle, alcényle, dicyanovinyle ou SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, où Z représente H ou un groupe alkyle en C_1 à C_{10}, un métal alcalin, un ammonium ou un alkylammonium;
Y est une fraction conjuguée, par exemple, N=N, CW=CW, CW=N ou N=CW, où W représente H, un groupe alkyle en C_1 à C_{10}, ou un groupe alcoxy en C_1 à C_{10}; et
m = 1 à 5; et

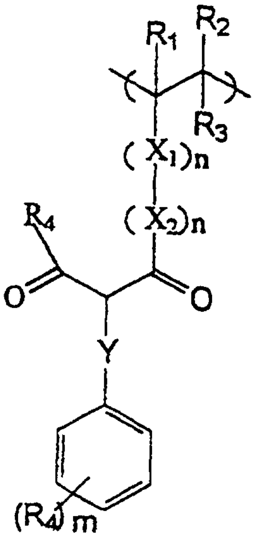
au moins un motif capable de réticuler le polymère ayant une structure



$$-\!\left(\begin{array}{cc} R_1 & R_2 \\ | & | \\ C & C \\ | & | \\ R_3 & G \end{array}\right)\!-$$

dans laquelle G contient une fonctionnalité de réticulation et R_1 à R_3 représentent, indépendamment les uns des autres, H, un groupe alkyle en C_1 à C_{10} ou un groupe alcoxy en C_1 à C_{10}; et
b) un solvant approprié.

2. Composition de revêtement anti-réfléchissant selon la revendication 1, dans laquelle le motif de colorant possède une structure:



dans laquelle R_1 à R_3 représentent, indépendamment les uns des autres, H, un groupe alkyle en C_1 à C_{10} ou un groupe alcoxy en C_1 à C_{10};
X_1 est C=O, OCO, CONH, O, un groupe aryle, alkyle en C_1 à C_{10}, cyclohexyle, pyridine ou pyrolidone;
X_2 est S, un groupe S-alkyle en C_1 à C_{10}, O, un groupe O-alkyle en C_1 à C_{10}, NH, un groupe N-alkyle en C_1 à C_{10} ; un groupe alkyle ou un groupe hydroxyalkyle en C_1 à C_{10};
n= 0 à 2;
R_4 représente H, un groupe alkyle en C_1 à C_{10}, un groupe alcoxy en C_1 à C_{10}, un groupe nitro, halogénure, cyano, aryle, alkylaryle, alcényle, dicyanovinyle ou SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, où Z représente H ou un groupe alkyle en C_1 à C_{10};
Y est une fraction conjuguée, par exemple, N=N, CW=CW, CW=N ou N=CW, où W représente H, un groupe alkyle en C_1 à C_{10}, ou un groupe alcoxy en C_1 à C_{10}; et
m = 1 à 5.

3. Composition anti-réfléchissante selon la revendication 1, dans laquelle le solvant comprend un mélange de solvants organiques.

4. Composition anti-réfléchissante selon la revendication 1, dans laquelle le solvant est choisi dans le groupe formé par l'éther monométhylique de propylèneglycol, l'acétate de l'éther monométhylique de propylèneglycol, le lactate d'éthyle, l'heptanone, la cyclopentanone, la cyclohexanone et la gamma-butyrolactone.

5. Composition anti-réfléchissante selon la revendication 1, dans laquelle le solvant comprend l'eau.

6. Composition anti-réfléchissante selon la revendication 1, dans laquelle le groupe de réticulation est choisi dans le groupe formé par les résidus carbodiimide, isocyanate, isocyanate séquencé, glycidylméthacrylate, alkylolacrylamide, alkylolméthacrylamide et méthylacrylamidoglycolate.

7. Composition anti-réfléchissante selon la revendication 1, dans laquelle Y dans le motif de colorant est une fraction azoïque.

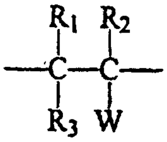
8. Composition anti-réfléchissante selon la revendication 1, dans laquelle le motif de colorant est compris dans la gamme d'environ 5 à environ 95 pourcent en moles et le motif de réticulation est compris dans la gamme d'environ 1 à environ 50 pourcent en moles du polymère.

9. Composition anti-réfléchissante selon la revendication 1, dans laquelle le polymère comprend de plus un ou plusieurs monomères vinyliques qui sont non absorbants et non réticulants.

10. Composition anti-réfléchissante selon la revendication 9, dans laquelle le monomère vinylique est choisi dans le groupe formé par l'anhydride maléique, les vinylacrylates, les vinylphénoliques, les éthers vinyliques, les vinylacrylamides, les acides carboxyliques de vinyle, les acides vinylsulfoniques et le N-(3-hydroxyphénylméthacrylamide).

11. Composition anti-réfléchissante selon la revendication 1, comprenant de plus au moins un motif dérivé d'un monomère vinylique hydrophile ou d'un monomère vinylique capable de devenir hydrophile.

12. Composition anti-réfléchissante selon la revendication 11, où le monomère vinylique hydrophile possède une structure:



dans laquelle R_1 à R_3 représentent, indépendamment les uns des autres, H, un groupe alkyle en C_1 à C_{10} ou un groupe alcoxy en C_1 à C_{10} et W est un groupe hydrophile.

13. Composition anti-réfléchissante aqueuse selon la revendication 12, dans laquelle le groupe hydrophile est choisi dans le groupe formé par les résidus $O(CH_2)_2$-O-(CH_2)-OH, $O(CH_2)_2$-OH, $(CH_2)_n$-OH (où n= 1 à 4), COO-(alkyle en C_1 à C_4), COOX, SO_3X (où X représente H, un métal alcalin, un ammonium, un alkylammonium), $CONHCH_2OH$.

14. Composition anti-réfléchissante selon la revendication 11, où le monomère vinylique hydrophile est choisi dans le groupe formé par l'anhydride maléique, l'anhydride fumarique, les vinylpyridines et les vinylpyrollidones.

15. Composition anti-réfléchissante selon la revendication 11, dans laquelle le motif de colorant est compris entre environ 5 et environ 95 pourcent en moles, le motif de réticulation est compris entre environ 1 et environ 50 pourcent en moles et le monomère vinylique hydrophile est compris entre environ 1 et environ 50 pourcent en moles du polymère.

16. Composition anti-réfléchissante selon la revendication 1, comprenant de plus un colorant.

17. Composition anti-réfléchissante selon la revendication 1, comprenant de plus un agent de réticulation.

18. Composition anti-réfléchissante selon la revendication 1, comprenant de plus un acide.

19. Composition anti-réfléchissante selon la revendication 1, comprenant de plus un acide engendré à chaud.

20. Composition anti-réfléchissante selon la revendication 19, dans laquelle l'acide est un ester diazonaphtoquinone d'une multihydroxybenzophénone.

21. Composition anti-réfléchissante selon la revendication 1, dans laquelle le polymère possède une masse moléculaire moyenne en poids dans la gamme d'environ 2 500 à environ 1 000 000.

22. Composition anti-réfléchissante selon la revendication 1, dans laquelle la teneur en ions métalliques dans le polymère est inférieure à 50 ppb de chaque ion métallique.

23. Procédé pour former une image sur un substrat comprenant les étapes consistant:

a) à revêtir le substrat avec la composition de revêtement anti-réfléchissante selon la revendication 1;
b) à chauffer le revêtement anti-réfléchissant;
c) à déposer une solution de photorésist sur le dessus du revêtement anti-réfléchissant;
d) à chauffer le revêtement de photorésist pour éliminer pratiquement tout le solvant du revêtement de photorésist;
e) à exposer selon une image le revêtement de photorésist;
f) à développer une image en utilisant un développateur aqueux basique;
g) éventuellement, à chauffer le substrat avant et après le développement;

h) à graver à sec le revêtement anti-réfléchissant.

24. Procédé selon la revendication 23, dans lequel la solution de photorésist comprend une résine novolaque, un composé photosensible et un solvant.

25. Procédé selon la revendication 23, dans lequel la solution de photorésist comprend un polyhydroxystyrène substitué, un composé photoactif et un solvant.

26. Procédé selon la revendication 23, dans lequel la solution de photorésist comprend un polyhydroxystyrène, un composé photoactif, un inhibiteur de dissolution et un solvant.

27. Procédé selon la revendication 23, dans lequel la température de chauffage pour le revêtement anti-réfléchissant est comprise entre environ 70°C et environ 250°C.

28. Procédé selon la revendication 23, dans lequel le développateur est une solution aqueuse d'hydroxyde basique exempt d'ions métalliques.